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14. ABSTRACT Autonomous buoyancy-driven gliders are becoming an increasingly important platform for the Navy for semi-continuous oceanographic observations and a host of applications. Glider systems in use suffer in flight performance from biofouling. We evaluated the coatings of the 3 glider types currently in use. Results from the lab assays showed, only the not-toxic CS#1 coating showed results comparable to the Silastic T2 PDMS standard. Results of water jet field testing showed no coatings performed as a true foul-release coating in comparison to the foul-release standard Intersleek. More effective antifouling coating on the gliders is recommended to improve flight performance.					
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EVALUATION OF GLIDER COATINGS AGAINST BIOFOULING FOR IMPROVED FLIGHT PERFORMANCE

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LONG-TERM GOALS

Autonomous buoyancy-driven gliders are becoming an increasingly important platform for the Navy for semi-continuous oceanographic observations. These observations are central to enhancing ocean model forecasting, underwater communications, underwater imaging, and a host of other applications. In order to provide these functions, it is critical that the flight characteristics be maintained for duration, spatial coverage and navigation. Currently, a number of the glider systems in use suffer in flight performance from biofouling, and this problem is exacerbated if the vehicle spends more time near coastlines or near the surface where there is enhanced biological activity. Here, we propose to leverage an existing ONR biofouling program (Code 34) to examine and evaluate the coatings of the 3 glider types currently in use. These evaluations will be compared to each other as well as the non-toxic coatings being evaluated under the biofouling program. These results have the potential to significantly increase the endurance and performance of gliders with direct benefits to the Navy.

OBJECTIVES

Our objectives are to examine a number of glider materials currently in use and evaluate their fouling (and anti-fouling) potential. The coatings will be evaluated using two assay approaches currently used by the ONR biofouling program to increase fuel/time efficiency for the Navy's active fleet. The final product from this program is to provide the glider users with an evaluation of their coating relative to other gliders and to other coatings. Information will help the current developers further optimize the flight performance of their systems.

Biofouling has proven to be a major cause of flight disturbance of Gliders. A collection of coatings and sections of other materials (wing, cowling, tail, etc.) currently in use on Gliders within the ONR program were tested in both the laboratory and field settings for efficacy against biofouling organisms. Results of these coatings were compared to results of standard control coatings tested within the ONR Biofouling program for down-select process to discover new non-toxic formulations.

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Laboratory assays are generally used within the ONR biofouling program to screen performance of coatings prior to field assessment. Coatings are assessed for toxicity using a leach assay, for antifouling behavior using a barnacle cypris larvae settlement assay and for foul-release properties using a barnacle removal assay. In addition, observations on the growth rate of barnacles and coating durability are recorded. Samples of coatings currently in use on gliders were prepared on slides and tested in the lab using these assays.

Static field testing is a more comprehensive assessment of the coatings' performance ability given that they are exposed to a diversity of species found in a natural fouling community. In the field coatings were evaluated for their efficacy as foul release and antifouling coatings using barnacle removal, water jet testing and percent coverage analysis. The Cal Poly static test site is located in Morro Bay, CA, which is equidistant from Los Angeles and San Francisco. The ocean is a cool temperate region and has a tremendous diversity of fouling species. The platform for testing is a floating dock with central wells through which panels are suspended. The panels remain at a constant depth of 2-3 feet below the surface. The temperature and salinity fluctuates seasonally from 11.2-22.3°C and 13-35‰. These data are measured every 15 minutes and are accessible at <http://www.slosea.org/about/dash.php>. Morro Bay's fouling community is diverse and changes seasonally. Barnacle recruitment usually occurs from summer to early fall and late winter to spring. The heaviest fouling occurs between spring and fall. The fouling community consists of sponges, tunicates, tubeworms, hydroids, anemones, tube-dwelling amphipods, arborescent and encrusting bryozoans, and several species of barnacles, the most abundant of which is *Balanus crenatus*. The most dominant fouling species is an invasive encrusting bryozoan, *Watersipora subtorquata*. A taxonomic database for species found in Morro Bay can also be found at <http://www.slosea.org/initiatives/is/invertdata.php>.

APPROACH AND WORK COMPLETED

Coatings were received from various ONR Glider operators (Table 1) by August 2010. Coatings for lab assays were either applied to glass microscope slides or materials were cut down to approximately the same size (1 x 3 in). Coatings for the field assessments were applied to 4 x 8 in panels or materials were cut to that approximate size. Lab assays were conducted between August and October, 2010. Coatings were deployed at the field site September 24th and were observed at approximately 1 month intervals over a six month period.

Laboratory assays

Leachate assay

All coatings were soaked for three days in 100 mL of seawater prior to the settlement assay. Samples of the leachate from each of the coatings were taken and used to conduct assays of survivorship with approximately 100 nauplii larvae of *Artemia* sp. (brine shrimp). The larvae were exposed to the coating leachate and their survival was monitored for 2 days. Survival of larvae in each coating leachate was compared to survival of larvae in the leachate from a glass slide control.

Settlement assay

Balanus amphitrite cypris larvae were obtained from the Duke University Marine Laboratory. A 400 µL drop of seawater containing 20-40 barnacle cypris larvae was placed on the surface of each coating replicate in a covered Petri dish. The larvae were placed in an incubator at 25°C with a 12 hour light/dark cycle and allowed to settle for 48 hours. At the end of the initial assay period the numbers of

individuals that successfully attached and metamorphosed were counted. Larvae that did not settle by the end of the 48 hour period were observed for signs of abnormal behavior to assess any compromises to normal physiological function. Settlement on each coating formulation was compared to settlement on the T2 controls.

Table 1 The list of test coatings and the corresponding Group letter assigned to each for testing.

Received from	Associates	Coating group	Coating type
Jeff Sherman (UCSD)	David Manly (Scripps)	A	Aluminum with Seahawk Mission Bay 4000 Series Zinc Omadine/Zinc Oxide paint
	Dan Rudnick (UCSD)	B	Aluminum with Proline 4800 paint
	Russ Davis (UCSD)	C	Aluminum with Proline 4800 paint with Zinc Oxide cream (desitin)
		D	Anodized 6061-T6 Aluminum with a duplex seal
		E	Aluminum with Seahawk 4000 with Bio-Boost additive
		F	Nitrile Rubber (SOLO Sleeve bladder)
		G	Fiberglass (Cowling)
		H	Conap TU-8080 Polyurethane (Tail)
		I	Conap TU-971 Polyurethane (Wing)
		J	Polypropylene
Hank Lobe (Severn Marine)	Clayton Jones (Webb)	K	CS#1: ClearSignal (slides) and CS#2: optically clear, ClearSignal (panels)
Craig Lee (Univ of WA)	Jason Gobat (Univ. of WA)	L	standard Seaglider paint
		M	standard Seaglider paint with Kiss Cote applied
		N	Seaglider (pieces of cut up glider)

Monitoring growth of juvenile barnacles and coating durability

Following attachment and metamorphosis the juvenile barnacles were fed and allowed to grow until they reached a size suitable for removal testing. During that time, barnacles were monitored for growth and any unusual observations, including reduced growth or mortality, were recorded. Coatings were also observed closely during this time and any defects or problems with the coatings were recorded.

Removal assay

Once the barnacles reached the appropriate size for removal testing, the basal plate of each barnacle was photographed and then each barnacle was removed from the slide and the maximum force of removal was recorded. During testing, each slide was clamped into a specialized chamber that sits below a force-gauge mounted on a motorized test stand allowing the slide to be immersed in seawater. This allowed us to test the force necessary to remove the barnacles in shear and in situ. Images were then analyzed using NIH's ImageJ to calculate the area of the basal plate for each barnacle. If barnacles were removed entirely from the surfaces, the critical removal stress (N/mm^2) was then

calculated and averages were compared against other coatings, as well as control groups. If the barnacles broke during removal testing, CRS could not be calculated because the force measured in that situation is the cohesive force of the barnacle and not the adhesive force of the barnacle basal plate to the substrate. If the barnacle's basal plate was partially removed, the remaining basal plate was photographed and the exact percentage remaining after testing was calculated (%BPR). The amount of basal plate remaining on a coating (%BPR) is an indicator of foul-release performance. Low percentages left indicate a relatively good coating whereas a high percentage remaining indicates a poor foul-release coating.

Field testing

Determination of Percent Coverage

Digital photographs of each panel replicate were taken at each visit. Percent coverage of cumulative soft and hard fouling organisms were visually estimated for each replicate on which water jet testing was not done. Visual estimates were made in the field and edges were blocked out to eliminate any part of the edge that may not be fully coated and eliminate growth due to settlement on the edges. Organisms categorized as "hard" fouling include barnacles, polychaete worms with calcareous tubes, encrusting bryozoans, molluscs and any other unidentifiable fouler with calcareous structures. Those categorized as "soft" fouling include macroalgae, cnidaria or hydrozoans, arborescent bryozoans, polychaete worms with tubes constructed of sediment, sponges, solitary and colonial tunicates, unidentifiable soft foulers without calcareous structures, as well as incipient foulers, which includes any newly recruited organism or those that are too small to be identified. All macrofouling (soft and hard foulers) are combined to show overall percent coverage on each panel (Figure 1).

Measurement of Biofouling Adhesion using a Water Jet

Adhesion of fouling organisms was measured using a water jet. The test apparatus consists of a modified SCUBA tank filled with seawater connected to another SCUBA tank filled with compressed air via a regulator hose, thereby allowing the water pressure leaving the tank to be controlled. A hose was connected to the pressurized water tank and had another regulator at the nozzle allowing water pressure to be controlled at the working end. The pressurized stream of water was applied to the surface of the panel through the nozzle at a series of water pressures (40, 80, 120, 180 and 240 psi). The water stream was applied perpendicular to and approximately 1 inch away from the surface as evenly as possible across the entire surface of the panel.

One replicate of each panel type was tested monthly using the water jet. Prior to testing, percent coverage of each fouling category (slime, soft or hard) was estimated and organisms present were recorded. Each panel was then sprayed at each of the water pressures listed above and percent coverage of each fouling category was roughly estimated after each pressure was applied. After the maximum pressure was applied organisms that still remained were also noted. Digital pictures were taken before and after water jet testing and are shown in the attached PowerPoint file. All pictures are also available for download at the following link, <http://marine.calpoly.edu/Brewer/Glider%20coatings/>.

Measurement of barnacle adhesion

The method used for measuring barnacle adhesion is based on ASTM D 5618-94, "Standard Test Method for Measurement of Barnacle Adhesion Strength in Shear" (Anonymous, 1997). A shear force was applied to the base of the barnacle using a hand held force gauge, at the rate of approximately 4.5 N s^{-1} . The force at which the barnacle detached from the surface was recorded. Basal diameters were measured in the field using calipers and were used to calculate the basal plate area. The critical

removal stress (CRS) was then calculated by dividing the force of removal by the surface area of the basal plate. Barnacles that broke upon removal leaving behind greater than 10% of their basal plate were not included in calculating CRS, but were recorded and used to help evaluate panel efficacy by calculating the percentage of broken barnacles of those on which removal was attempted. Those with high percentage of barnacle breakage were not functioning as foul release coatings.

Visual Inspection of coating durability

A visual inspection of each coating was also done to observe any signs of damage or degradation. Observations recorded include the type of damage, approximate severity and estimated area affected. Due to the nature of the fouling community this is sometimes difficult to assess but every effort is made to identify defects. Most often, defects are observed on panel replicates used for water jet testing not only because it is easier to observe the entire surface when the organisms have been cleared away but also because the water jet testing itself may actually be responsible for some of the defects.

RESULTS

Laboratory Assays

Leachate assay

Results of the leach and settlement assay are shown together in Figure 1 for easy comparison. There was a significant difference in average mortality of brine shrimp in the leach assay (Kruskal Wallis $p=0.0002$). Post hoc testing was not done for each comparison but it is clear which of the coatings had higher mortality than the glass control; namely the Aluminum with Seahawk Mission Bay 4000 series with and without the Bio-Boost additive (A and E, respectively), and the Anodized 6061-T6 Aluminum with a duplex seal (D). These coatings showed higher mortality of brine shrimp as well as 100% mortality of cypris larvae during the settlement assay which indicated the coatings were toxic. The fiberglass cowling (G), Polypropylene (J), and standard Seaglider (L) samples showed slightly increased mortality of brine shrimp compared to the glass control; however these did not inhibit settlement and were evidently not toxic to the cypris larvae. All other coatings showed brine shrimp mortality comparable to or lower than the glass control.

Settlement assay

There was also a significant difference in average settlement of cypris larvae between coatings (Kruskal Wallis $p<0.0001$). Again, post hoc testing was not done for each comparison but it is clear which were significantly different than the controls. The following coatings had settlement averages comparable to the intersleek control and therefore did not exhibit any antifouling characteristics; aluminum with Proline 4800 paint (B), CS#1 ClearSignal coating (K), fiberglass cowling (G), polypropylene (G), and the standard Seaglider paint with and without applied kiss cote (L and M, respectively). In addition to the coatings previously noted as toxic to both brine shrimp and cypris larvae (G, J and L), the following coatings showed complete mortality of cypris larvae only; aluminum with Proline 4800 with applied Desitin (C) and the Nitrile Rubber (SOLO sleeve bladder) (F). The pieces of the cut up glider with Seaglider paint (N) had zero settlement simply due to our assay not working on the thick curved metal surfaces. The settlement on each of the polyurethane tail and wing samples (H and I, respectively) were very low, yet the cyprids were alive, supporting that these coatings were not toxic.

Monitoring growth of juvenile barnacles and coating durability

Of the coatings that had barnacle settlement, most of them were observed to have comparable growth rates. However, growth was inhibited on the polyurethane tail and wing samples and within a few

weeks all the barnacles growing on them had died. The toxicity may have been low enough to allow them to settle but prevented them from growing well over a longer period of time.

None of the coatings were observed to have any defects during the lab assays.

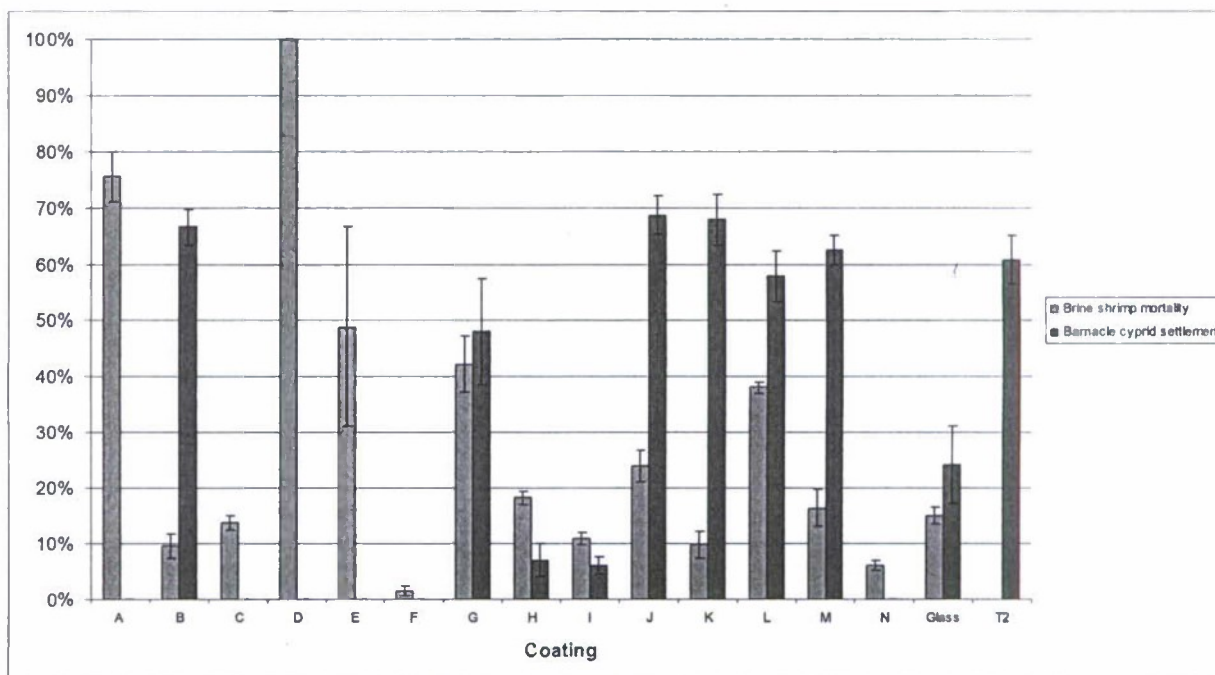


Figure 1. Average percent mortality of brine shrimp (blue) exposed to coating leachate samples and percent settlement of barnacle cypris larvae (burgundy) on experimental coatings. Error bars represent one standard error of the mean.

Removal assay

Removal testing was completed on all coatings that had barnacles growing on them after the settlement and grow-out period (see Table 3 for summary of results for all coatings). It was not possible to test coatings that showed zero settlement or on coatings where barnacles died during the grow-out period. Of the barnacles that were removed from coatings, most of them left 100% of their basal plate behind. When this occurs, it indicates that the cohesive strength of the barnacle was less than the force necessary to remove the entire barnacle from the coating. It is also a clear indication that the coatings are not functioning as a foul-release surface. The CS#1 ClearSignal coating was the only coating that showed foul-release characteristics (Table 2). The average percentage of basal plate remaining (%BPR) was about 37%, which indicates a relatively good foul-release surface. Although the percent of individuals that were completely removed was significantly lower than our internal standard (24% and 62%, respectively), the average CRS value for those individuals that were removed was not statistically different from the average CRS of the T2 controls (ANOVA $p = 0.1379$), our internal lab standard for an excellent foul-release surface.

Table 1 Comparison of barnacle removal results between CS#1 coating and the T2 standard.

Coating	Ave CRS (N/mm ²)	Ave %BPR	% removed completely
CS#1	0.121	37.2%	23.5%
T2	0.115	18.2%	61.9%

Table 2 Summary of results for lab testing on all coatings. For leach results, significant = higher mortality than glass and indicates toxicity. For settlement, significant = lower settlement than the T2 control and indicates settlement inhibition. For removal, 100% BPR means the coating is not functioning as a foul-release surface.

Coating	Notes	Leach Results	Sett Results	Removal results
Aluminum with Seahawk Mission Bay 4000 Series Zinc Omadine/Zinc Oxide paint (A)		significant	0-complete mortality	not tested due to mortality
Aluminum with Proline 4800 paint (B)		not significant	high-not significant	100% BPR on all
Aluminum with Proline 4800 paint with Zinc Oxide cream (Desitin) (C)	apply desitin to surfaces of slides	not significant	0-complete mortality	not tested due to mortality
Anodized 6061-T6 Aluminum with a duplex seal (D)		significant	0-complete mortality	not tested due to mortality
Aluminum with Seahawk 4000 with Bio-Boost additive (E)		significant	0-complete mortality	not tested due to mortality
Nitrile Rubber (SOLO Sleeve bladder) (F)	irregular shapes may affect testing	not significant	0-complete mortality	not tested due to mortality
Fiberglass (Cowling) (G)	irregular shapes may affect testing	significant	high-not significant	100% BPR on all
Conap TU-8080 Polyurethane (Tail) (H)	irregular shapes may affect testing	not significant	low-significant	not tested due to mortality
Conap TU-971 Polyurethane (Wing) (I)	irregular shapes may affect testing	not significant	low-significant	not tested due to mortality
Polypropylene (J)		significant	high-not significant	100% BPR on all
CS#1:ClearSignal (K)		not significant	high-not significant	CRS & %BPR comparable to T2
standard Seaglider paint (L)		significant	high-not significant	100% BPR on all
standard Seaglider paint with Kiss Cote applied (M)		not significant	high-not significant	100% BPR on all
Seaglider? (N)	cut up glider, irregular shapes may affect testing	not significant	0-incompatible with assay	not tested due to lack of settlement

Field Testing

Determination of Percent Coverage

Panels were immersed on September 24th 2010 and inspections were done at approximately one month intervals over a six month period. Fouling accumulation was relatively low on all panels during the first few months of submersion and then gradually increased to higher percent coverage in the last few months (Figure 2). This was the expected trend since it takes time once organisms settle for them to

spread out and colonize the entire panel. During the first month the Aluminum with Seahawk Mission Bay 4000 series with and without the Bio-Boost additive (A and E, respectively) almost completely inhibited growth of macrofouling, but it increased gradually during the remaining months. Both of these coatings showed toxicity in the lab testing so this result was consistent with those findings, although the toxicity decreased over time and fouling increased. In general, most of the coatings tracked closely with the Intersleek control shown in red (Figure 2). In our experience fouling on a standard ablative copper coating is generally less than 20% over a 6 month period shown in black (Figure 2). None of the coatings tested in this assay had less than 50% fouling and most had more than 70% fouling, indicating they were not functioning as well as the Navy's standard copper ablative coating.

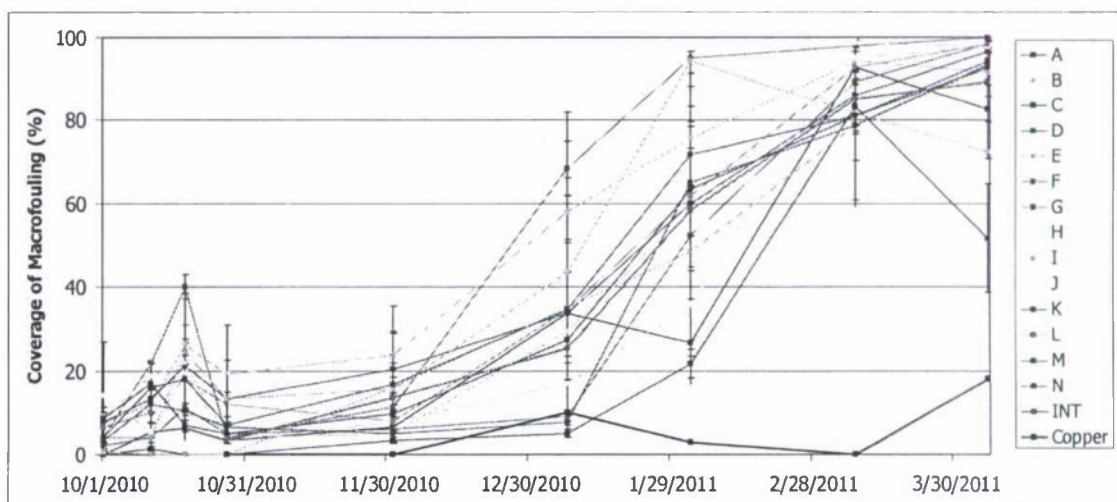


Figure 2. The percent coverage of macrofouling organisms over the duration of submersion at the Cal Poly test site. Percentages were averaged from 3 replicate panels and do not include the panel used for water jet testing. Error bars represent one standard error of the mean.

Measurement of Biofouling Adhesion using a Water Jet

Results of the water jet testing on coatings are summarized in Table 2. The values listed in the table are differences in estimated panel coverage that remained after the highest water pressure was applied between the test panel and the Intersleek standard. Values highlighted in green represent panels with removal that was equivalent to or better than the Intersleek standard with respect to each fouling type. Values highlighted in yellow were slightly less effective ($\leq 10\%$ greater coverage than Intersleek) and those highlighted in orange were much less effective as foul-release coatings ($> 10\%$ coverage than Intersleek). In general, removal of slime and soft fouling organisms was comparable to or only slightly less than the Intersleek control each month. Removal of hard fouling organisms was slightly less on several panels in the first few months but by month seven was poor in comparison on most panels.

Measurement of barnacle adhesion

We were unable to get any measurements of barnacle removal in the field for a variety of reasons. If barnacles had settled on coatings, many of them did not reach a size suitable for testing or were already dead when found on some of the slightly toxic coatings [specifically noted on Nitrile Rubber-SOLO sleeve bladder (F) and Conap TU-971 Polyurethane wing (I); both of which showed mortality of barnacles with prolonged exposure in the lab assay]. Barnacles were observed penetrating through the coating of the Aluminum with Seahawk 4000 with Bio-Boost additive (E) and attaching to the

substrate beneath. Barnacles were not observed on any of the CS#2 (K) ClearSignal panels so we were unable to confirm the positive foul-release results seen in the lab barnacle removal assay.

Table 2 Water jet removal results for test panels at 1, 4, and 7 months of submersion. Values are the differences in coverage between each test panel and the Intersleek standard that remained on the panel after the highest water pressure was applied. Zero indicates no difference, negative values indicate less % coverage remaining than the Intersleek standard and positive values indicate greater % coverage than the Intersleek standard.

Date	Oct. 27, 2010			2-Feb-11			31-May-11		
Panel	Slime	Soft	Hard	Slime	Soft	Hard	Slime	Soft	Hard
A	-30	0	0	-25	0	0	-25	0	35
B	-25	0	5	10	0	5	-50	0	60
C	-25	0	0	-45	-5	-5	-40	0	5
D	-25	5	5	-10	0	10	-55	0	50
E	-30	0	0	-25	0	0	-30	0	50
F	-25	5	5	-10	0	0	-55	0	10
G	-30	0	0	0	0	0	-50	0	70
H	-25	0	0	0	0	0	0	0	5
I	-25	5	5	0	5	5	-55	0	45
J	-25	0	5	5	0	0	15	0	5
K	-25	5	5	-10	-5	0	-45	-5	15
L	-25	0	5	-5	0	0	-10	0	25
M	-25	5	5	-10	0	0	-20	0	35
N	-20	5	5	-10	0	0	-20	0	25

Visual Inspection of coating durability

By the January visit, two replicates of coating K were delaminating from the panel used for fouling observations and approximately 10% of the coating had detached from the replicate used for water jet testing. By the April visit, the area of the coating that was missing on the water jet panel had increased to approximately 30% (clearly visible in the pictures on the attached PowerPoint file). Also, as mentioned above barnacles were cutting through the surface of the Aluminum with Seahawk 4000 with Bio-Boost additive (E). No defects were observed on any of the other test panels.

IMPACT/APPLICATIONS

Results from the lab assays showed that several of the coatings were toxic to brine shrimp, cypris larvae, and/or juvenile barnacles. Of the coatings that were not toxic, all of them showed high settlement and most of those showed poor foul release. Only the CS#1 coating showed results for barnacle removal that were comparable to the Silastic T2 PDMSe standard, which functions as a good foul-release surface. Results of water jet testing in the field showed relatively good results for several of the panels in the first three to four months, but results were poor for most coatings by the fifth month and beyond with large amounts of hard fouling remaining on most panels (see Table 2 and Figure 2). The significant presence of hard fouling organisms remaining could drastically alter glider flight performance. Results of water jet testing are difficult to interpret when looking at the table alone since the values shown are a snapshot of what remains and does not quantify removal of fouling organisms. By looking at the pictures as well is it easier to see how they performed. The aluminum

with Proline 4800 with applied Desitin (C) seemed to have relatively good results but this was due to limited growth to begin with due to the Desitin cream. As was requested these panels had a layer of Desitin cream smeared across the surface which inhibited growth of everything except some slime. When these panels were sprayed with the water jet the Desitin was washed away a little at a time and in areas of the panel where it completely washed away performance was poor. The Desitin worked for a period of time to prevent growth but would not be ideal for applying to a large area because it would affect glider performance in the same ways the fouling does and it wears off relatively fast even without applied water pressure. It may be useful for applying to small sensitive areas where its impact would be minimal. The Nitrile Rubber-SOLO sleeve bladder (F) also seemed to do well but this was also due partially to limited growth due to toxicity, and differences in removal may be due to the flexibility of that material. Finally, the Conap TU-8080 Polyurethane tail (H) also showed good results, but again these were due to limited growth. This material also showed inhibition of growth in the lab testing with complete mortality within a few weeks post settlement. In summary, none of the coatings or materials tested performed as a true foul-release coating in comparison to our foul-release standard Intersleek. Some of the coatings or materials tested had slight antifouling performance but none of them inhibited growth as well as the standard ablative copper coating. In addition, it has been reported that foul-release coatings are only effective when a vessel achieves higher speeds which may be unattainable by gliders. Therefore our recommendation is to use a more effective antifouling coating on the gliders to prevent fouling accumulation while they are under way.

TRANSITIONS

None to date

RELATED PROJECTS

Marine Biofouling: Community Structure and Surface Interactions Program (Code 34) (PI: D. Wendt)

PUBLICATIONS

None.

HONORS/AWARDS/PRIZES

Arctic Fulbright Chair (2011-2012) – Mark A. Moline